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WASTE MANAGEMENT ANALYSIS FOR THE NUCLEAR FUEL CYCLE

I. ACTINIDE RECOVERY FROM AQUEOUS SALT WASTES

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SUBJECT DESCRIPTORS

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CONTENTS

Abstract	1
Introduction	1
Experimental	2
Materials	2
Procedures	3
Results and Discussion	3
Properties of Bidentate Extractant	3
Actinide Removal From Salt Waste	7
Summary and Conclusions	8
References	8

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WASTE MANAGEMENT ANALYSIS FOR THE NUCLEAR FUEL CYCLE

I. ACTINIDE RECOVERY FROM AQUEOUS SALT WASTES

Larry L. Martella and James D. Navratil

Abstract. A preliminary feasibility study of solvent extraction methods has been completed for removing actinides from selected salt wastes likely to be produced during reactor fuel fabrication and reprocessing. The use of a two-step solvent extraction system, tributyl phosphate (TBP) followed by a bidentate organophosphorus extractant (DHDECMP), appears most efficient for removing actinides from salt waste. The TBP step would remove most of the plutonium and >99.99% of the uranium. The second step, using DHDECMP, would remove >99.91% of the americium, the remaining plutonium (>99.98%), and other actinides from the acidified salt waste.

INTRODUCTION

The U. S. Energy Research and Development Administration (ERDA) initiated a major research and development program to close the light water reactor (LWR) fuel cycle; this program is being continued by the U. S. Department of Energy (DOE). The program comprises efforts by both DOE facilities and industry to (1) provide the technology and design for fuel recycling facilities and (2) to determine the economic and environmental impact of recycling.

Reprocessing nuclear fuel elements generates liquid and solid radioactive wastes that must be converted to forms that can be transported and stored. A program consisting of experimental and computational tasks was assigned to Oak Ridge National Laboratory (ORNL). The assigned tasks were for the development of a cost-risk-benefit analysis of actinide partitioning and transmutation as a waste management concept. The program has been defined by ORNL¹ and a preliminary assessment has been made.²

The principal emphasis of the ORNL program will be to evaluate partitioning. In this approach, long-

lived and biologically significant nuclides are recovered (partitioned) from waste streams produced within the nuclear fuel cycle. These nuclides may then be recycled to either the fuel cycle or to special reactors for transmutation and fission to shorter-lived, less biologically significant radionuclides. Successful partitioning could reduce the need for long-term storage of fission products to 10^3 years, in addition to recovering actinides for recycle.³

Because of the recognized need for an early assessment of the partitioning-transmutation concept, the program is limited to applied, rather than basic, research and development.

The program has been divided into three groups of tasks. One group is composed largely of experimental work concerned with separations; the other two groups are concerned with nonpartitioning aspects of the program. In the first group, there are nine subtasks: (1) actinide recovery from solids, (2) Am-Cm recovery using bidentate extractants, (3) Am-Cm recovery using inorganic ion exchange media, (4) recovery alternatives applicable to waste streams, (5) actinide recovery from combustible waste, (6) actinide recovery and recycle preparation for waste streams, (7) radiation effects, (8) thermal transmutation studies, and (9) risk-benefit analysis.

Subtasks 5 and 6 have been the responsibility of Rocky Flats. Progress on both subtasks has been reported,^{4, 5} and the experimental programs for Subtask 6 have been completed.

The purpose of Subtask 6 is to determine the feasibility of removing actinides from secondary aqueous waste streams that are likely to be produced during reactor fuel fabrication and reprocessing. The waste streams are part of two proposed flow sheets titled "Salt Waste Management" and "Acid and Waste Water Management."² Results

TABLE 1. Gas Chromatography - Mass Spectroscopy (GC/MS) Analysis of Impure and Purified DHDECMP^a

Component	Impure (%) ^b	Purified (%) ^b
diethylamine	0.1	0
decane	0.3	0
undecane	0.3	0
dichloro-N,N-diethylacetamide	0.7	0.3
α ,diethylamino-N,N-diethylacetamide	2.4	0.2
unidentified components	3.9	1.8
hexylchloride	2.5	0.7
chloro-N,N-diethylacetamide	3.0	0.5
dihexylphosphite	4.1	0
dihexylmethylphosphite	7.8	7.5
triethylphosphate	27.9	26.0
dihexyl-N,N-diethylcarbamoylmethylenephosphonate	47.0	63.0

a. Dihexyl-N,N-diethylcarbamoylmethylenephosphonate purified by Amberlyst® A-26 resin treatment.

b. Relative peak area of GC/MS.

of work on salt waste management are described in this report. Work on acid and wastewater management is described in Part II of this series of reports.⁶

EXPERIMENTAL

Materials

The bidentate organophosphorous extractant, dihexyl-N,N-diethylcarbamoylmethylene-phosphonate (DHDECMP), was obtained in impure (~50%) form from Wateree Chemical Company, Lugoff, South Carolina. Impure DHDECMP contains an impurity that prevents efficient stripping of actinides at low acidity.

The impurity was removed by an ion-exchange process adopted from a method to purify tributyl phosphate.⁷ The process consisted of passing 30 vol % DHDECMP-CCl₄ (carbon tetrachloride) through a bed of Amberlyst® A-26 (a macro-

reticular, strong-base, anion-exchange resin) in the hydroxide form. The impurity was sorbed on the resin. The resin then was regenerated by washing with 3M HNO₃, water, 2M NaOH, and water again before being dried with acetone. An analysis of the DHDECMP before and after purification is shown in Table 1.

Actinide feed solutions were prepared from purified stock solutions of americium, uranium, and plutonium. All solutions contained >0.35M HNO₃.

A synthetic salt waste solution was prepared by combining an incineration liquor and analytical waste² (Table 2) and then acidifying it with 7M HNO₃. The acidification process required care because considerable foam and heat were produced. Filtration after acidification indicated that no solids were present in the waste.

Deionized water was used in all cases; all other chemicals were reagent grade.

*Product of the Rohm and Haas Co., Philadelphia, Pa.

TABLE 2. Composition of Synthetic Basic Wastes Prior to Acidification

Component	Concentration
Incinerator Liquor	
Na_2CO_3	1.36M
Na_3PO_4	0.46M
NaCl	0.52M
Na_2SO_4	0.37M
NaNO_3	0.07M
Pu	0.0002M
Am	0.00002M
U	0.02M
Fission products (synthetic)	0.14 g/l
Analytical Waste	
HNO_3	1.3M
HCl	0.1M
NaNO_3	0.005M
$\text{K}_2\text{Cr}_2\text{O}_7$	0.005M

NOTE: Acidified salt waste composed of 22 vol % incinerator liquor, 2 vol % analytical waste and 76 vol % 7M HNO_3 . (See Reference 2.)

Procedures

Distribution coefficients (D) were determined by equilibrating equal volumes of actinide feed solutions and extractant. After phase separation, the aqueous phase was analyzed for HNO_3 and actinide concentration. Other extraction and back-extraction (stripping) experiments were made by equilibrating aqueous and organic phases at specified aqueous-to-organic (A/O) ratios followed by phase separation and analysis.

Nitric acid concentration was determined by acid-base titration. Uranium concentration was determined by fluorometric techniques, and plutonium and americium concentrations were identified by radiometric counting methods. Plutonium, in the presence of salt and americium, was determined by pulse-height radiometric analysis

after isotopic dilution and solvent extraction separation.

RESULTS AND DISCUSSION

Figure 1 presents a conceptual flow sheet for salt waste management.² Although fuel reprocessing waste streams are shown, it is envisioned that the salt wastes from a fuel fabrication plant could be treated in a similar manner. The cooling water will be sent to water purification, whereas it will be necessary to treat the tributyl phosphate (TBP) scrub by another process or to remove TBP hydrolysis products prior to treatment.

Three experimental approaches were planned for processing salt wastes free of TBP hydrolysis products: bidentate extraction, combined tributyl phosphate-bidentate extraction, and cation exchange. Testing of solvent extraction processes for determining the feasibility of removing actinides from salt waste streams was completed. The extractant, DHDECMP, was evaluated in a batch contactor. No work on cation exchange was done.

Properties of Bidentate Extractant

Impure (~50%) DHDECMP contains an impurity that prevents efficient stripping of actinides at low acidity. The impurity was removed by resin treatment. Table 3 shows americium distribution coefficients (D) of the DHDECMP before and after impurity removal. (D = ratio of solute concentration in the organic phase to americium concentration in the aqueous phase at equilibrium). It is apparent from the D values that at low HNO_3 concentrations especially, the impurity in the DHDECMP prevents any stripping of americium from the organic phase.

Distribution coefficients for thorium, uranium, plutonium, and americium versus nitric acid concentration are plotted in Figure 2. The results are in fair agreement with work by Schulz and McIsaac,⁸ even though the purity of the DHDECMP is different. The data show that the actinides can be extracted from strong nitric acid solution. For back-extraction of the actinides at low acidity, thorium and americium pose no problem. Plutonium can be

FIGURE 1. Conceptual Flow Sheet for Salt Waste Management

TABLE 3. Effect of DHDECMP^a Purity on Americium Distribution Coefficients(Am D^b values in various concentrations of DHDECMP^c)

HNO ₃ (M)	DHDECMP Purified	(vol %)			
		30	50	70	100
0.35	Yes	0.09	0.42	1.3	3.3
0.35	No	125	—	—	116
7.0	Yes	1.9	15	43	53
7.0	No	5.5	—	—	68

a. DHDECMP - dihexyl-N,N-diethylcarbamoylmethylene-phosphonate

b. D - distribution coefficient

c. Estimated accuracy $\pm 25\%$. DHDECMP diluted with carbon tetrachloride. Distribution coefficient (D) is the ratio of solute concentration in the organic phase to solute concentration in the aqueous phase at equilibrium.

FIGURE 2. Effect of Nitric Acid Concentration on Actinide Extraction for 30 Volume Percent DHDECMP*-CCl₄

*DHDECMP, dihexyl-N,N-diethylcarbamoylmethylenephosphonate

FIGURE 3. Stripping of Uranium From Two Extraction Systems With Water

FIGURE 4. Evaluation of Uranium Stripping With 30% DHDECMP*-CCl₄ (Aqueous-to-Organic Ratio = 1)

*DHDECMP - dihexyl-N,N-diethylcarbamoylmethylene phosphonate

stripped as easily as americium by reduction to the trivalent state.⁸ Uranium appears to be the only actinide that would cause problems in stripping with water or dilute nitric acid.

Uranium stripping from 20 vol % DHDECMP-DIPB (diisopropylbenzene) was compared to 30 vol % TBP-dodecane using water as the stripping agent. Uranium-loaded extractants were repeatedly contacted with water using an aqueous-to-organic ratio (A/O) of five. Uranium concentration in the aqueous strip solutions was determined to construct Figure 3.

Figure 3 shows a plot of percent uranium stripped from the two extractant systems versus the number of contacts. Results show that the TBP-dodecane system permits the fastest stripping of uranium while the DHDECMP extraction systems retain uranium. The leveling off of uranium removal with the DHDECMP indicates perhaps the presence of an impurity in the DHDECMP that has a high affinity for uranium. Other stripping agents (Figure 4) did not significantly improve uranium stripping (>85%) compared to water stripping.

Actinide Removal From Salt Waste

Plutonium extraction from various acidified salt waste solutions was investigated. One batch of acidified solution was not treated and was used as a control. A second batch was boiled for one hour. A third acidified solution was boiled for one hour, adjusted to 0.1M Fe(II) with 3M ferrous sulfamate, and had sodium nitrite added. A fourth batch was adjusted to 0.1M F⁻ with concentrated hydrofluoric acid, boiled for one hour, and adjusted to 0.1M Al³⁺ with an acidified, concentrated solution of aluminum nitrate.

The four acidified waste salt solutions were each equilibrated 7 times with 20 vol % DHDECMP - 30 vol % TBP - 50 vol % DIPB (A/O = 5). After the fourth and seventh contact, the aqueous phase was analyzed for plutonium. Results of the plutonium analyses are shown in Table 4.

The results show no difference between the acidified salt waste and the solution that was boiled. Compared to these two solutions, more plutonium was removed from the solution in which the plutonium valency was adjusted (Fe²⁺, NO₂⁻), and significantly more plutonium was removed from the solution treated with fluoride to destroy plutonium polymer.

TABLE 4. Plutonium Removal From Various Acidified Salt Waste Solutions With 20 Vol % DHDECMP^a - 30 Vol % TBP^b-DIPB^c

Initial Plutonium Concentration: 120 mg/l

Temperature: 22-24 °C

Estimated Accuracy: ±20%

Acidified Waste Treatment	Plutonium Content After 4 Contacts		Plutonium Content After 7 Contacts	
	(mg/l)	(%)	(mg/l)	(%)
No treatment	0.10	0.08	0.05	0.04
Boiled	0.10	0.08	0.05	0.04
Boiled, Fe ²⁺ and NO ₂ ⁻ added	0.08	0.07	0.02	0.02
F ⁻ added, boiled, Al ³⁺ added	0.02	0.02	(d)	(d)

a. DHDECMP - dihexyl-N,N-diethylcarbamoylmethylenephosphonate

b. TBP - tributyl phosphate

c. DIPB - diisopropylbenzene

d. Not determined

The problem of removing actinides, especially plutonium from salt waste, was evaluated using both TBP and DHDECMP extraction schemes. Figure 5 presents the plutonium and americium analyses of acidified salt waste after consecutive contacts with 30 vol % TBP-dodecane and 30 vol % DHDECMP-CCl₄. An aqueous-to-organic ratio of 5 was used. The results show that DHDECMP was more efficient than TBP in removing plutonium. Uranium concentration in the salt waste was reduced from 1 g/l to $>7 \times 10^{-5}$ g/l after 10 contacts with 30 vol % TBP-dodecane.

These results and those in Table 5 show that the solvent extraction systems are capable of removing >99.99% of the uranium, >99.98% of the plutonium, and >99.91% of the americium from the acidified salt waste.

SUMMARY AND CONCLUSIONS

A preliminary evaluation was completed of methods to remove actinides from selected aqueous salt waste streams likely to be produced during reactor fuel fabrication and reprocessing. Feasibility runs were made with two solvent extractants, TBP and DHDECMP, to remove actinides from synthetic salt waste. One extractant, DHDECMP, effectively removed actinides, but uranium stripping was

inefficient. More efficient uranium stripping agents than water were not found; however, McIsaac reported oxalic acid as an effective uranium stripping reagent.⁹ The TBP extractant effectively removes 99.99% of the uranium and most of the plutonium. Trivalent actinides are not removed with TBP.

The use of a two-step solvent extraction system, TBP followed by DHDECMP extraction, appears the most efficient for removing actinides from salt waste. The TBP step would remove most of the plutonium and >99.99% of the uranium. The second step, using DHDECMP, would remove >99.91% of the americium, the remaining plutonium (>99.98%), and other actinides from the acidified salt waste.

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FIGURE 5. Results of Actinide Removal With TBP* and DHDECMP**

*TBP - tributyl phosphate

**DHDECMP - dihexyl-N,N-diethylcarbamoylmethylenephosphonate

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TABLE 5. Actinide Removal From Acidified Salt Waste After Consecutive Contacts With a Bidentate Extractant

Number of Contacts ^a	Percent Pu Removed ^b	Percent Am Removed ^c
2	99.89	90.90
4	99.96	98.91
6	99.97	99.60
8	99.98	99.91

a. Aqueous-to-organic ratio of five.

b. 20 vol % DHDECMP (dihexyl-N,N-diethylcarbamoylmethylenephosphonate) - 80 vol % DIPB (diisopropylbenzene).

c. 50 vol % DHDECMP - 50 vol % DIPB.

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